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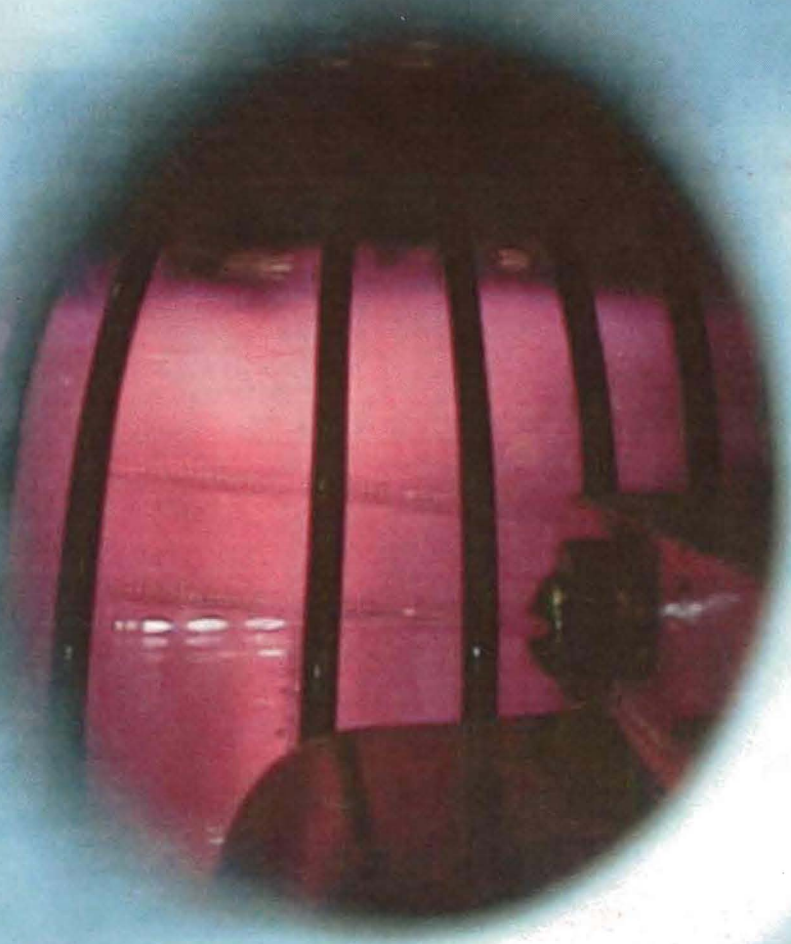

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An Overview of Plasma Processes

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Chapter 13 from 50 Years of Vacuum Coating Technology and the growth of the Society of Vacuum Coaters, Donald M. Mattox and Vivienne Harwood Mattox, eds., Society of Vacuum Coaters, 2007

Introduction

Plasmas have long been associated with vacuum coating. What would become known as "physical vapor deposition" was observed and noted in the discharge studies of W.M. Grove and M. Faraday in the mid 1800s. It is well known now that a plasma is a source of ions that can be accelerated under an electric field to high kinetic energies, and those energetic ions cause sputtering. The chemistry of plasmas has also had a long history. In the early part of last century, a number of researchers were investigating carbon-containing film deposition from organic vapors in discharges. It was not until much later, however, that plasmas became of interest to the vacuum coating community due to their unique abilities to both promote chemical dissociation and reactions in the gas phase and also deliver energetic ions and reactive species to surfaces. Consider a common process like reactive sputter deposition of titanium nitride, where the dissociation of the nitrogen background provides reactive atomic species that, along with sputtered titanium, form titanium nitride compounds at substrate surfaces. The flux of energetic ions leaving the plasma will liberate target material and, at the substrate, serve to increase film quality.

Plasma chemistry and surface reactions have become more complex with the desire to develop new films and functionalized surfaces. The problems associated with developing new materials are a prime concern in the commercialization of many plasma-based processes, and an understanding of the various plasma properties and processes is an essential first step.

Plasma Properties

What is a Plasma?

A plasma is an ionized gas where the number of negatively charged species is approximately equal to the number of positively charged species. This definition is very close to the meaning given by Irving Langmuir when he first introduced the term and encompasses a wonderfully broad range of physical descriptions covering both man-made and naturally occurring plasmas. Plasmas are often characterized by their charge density, degree of ionization, and average electron energy. For all known plasmas, the range over which these metrics vary is extraordinary: upward of 24 orders of magnitude in density and about 8 orders of magnitude in both electron energy and degree of ionization. Not surprisingly, the important physical and chemical considerations depend strongly on these various metrics. Similarly, the gas pressure is a strong factor in these considerations. For this chapter however, the focus will be on plasmas that have an important historical tie to vacuum coating and the processing of materials, which includes a much narrower range of the characteristics listed above.

Characteristics of Processing Plasmas

The plasma density is the number of negative or positive charges per unit volume. More commonly, plasma density refers to the electron density and is simply called the plasma density. The degree of ionization is obviously related to the plasma density but it also depends on the operating pressure and is defined by the ratio of charged-particle density to neutral-particle density. The average electron energy is commonly expressed in terms of electron temperature (T_e) and is measured in electron volts (eV).

Plasmas used in the processing of materials have densities in the range of 10^9 to 10^{12} cm^{-3} and electron temperatures in the 1 to 5 eV range. Unless otherwise stated, the units of eV and cm^{-3} will be used when referring to the electron temperature and plasma density in this chapter. The discussion also will be limited to pressures between 1 and 500 mTorr and to a degree of ionization that ranges from 10^{-6} to 0.1. It is important to note that processing plasmas are often called "non-equilibrium plasmas" because the electron temperature is greater than both the ion and gas temperatures, both of which are approximately room temperature. The breadth of processing plasmas are not limited to the ranges indicated. For example, there is interest in processing at atmospheric pressures, and in arc deposition, plasma densities can exceed 10^{14} cm^{-3} with a degree of ionization above 50%. Nonetheless, the range considered here covers most processing conditions.

The Sheath

Plasmas are often called quasi-neutral because the positive and negative charge densities nearly cancel. However, on small spatial scales and where plasmas interact with a surrounding wall, they are not charge-neutral. A plasma-wall interface is schematically represented in Figure 1.

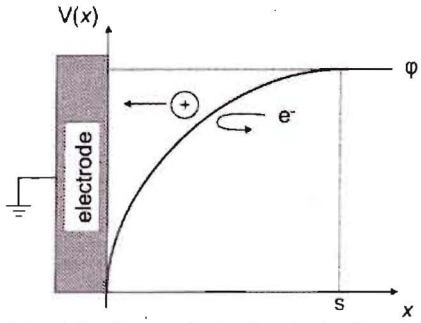

Figure 1. The plasma-surface interface showing the potential as a function of distance from a grounded electrode. The potential falls over the length of the sheath (s), starting at the plasma potential (φ) and decreasing to zero. The resulting electric field thus retards electron flow but enhances ion flow toward the electrode.

To understand this interface, remember that the electron is the dominant negative charge carrier in most plasmas, and it is much less massive than the ion (an electron weighs only 1/1823 amu). This means that electrons will respond much faster to applied electric fields and local charge imbalances. Electrons are also much more energetic than the ions and will leave the plasma at a faster rate than the ions, causing the plasma to acquire a net positive charge with respect to the walls, which tends to retard electron loss and enhance ion loss. A charge separation occurs over a thin region called the sheath. The sheath is dominated by positive ions and strong electric fields. The lack of electrons results in the characteristic dark space that is often observed near electrodes because there are few excitations. The electric field within the sheath produces a plasma potential, and this potential with respect to the wall is usually positive, independent of the wall potential. In processing plasmas, the plasma potential is roughly 3 to 5 times the electron temperature, which suggests a potential of 3 to 25 eV.

Debye Length

In all plasmas, there exists a characteristic length, called the Debye length, which is given by:

$$l = 743\sqrt{\frac{T_e}{n}},$$

where the Debye length is in cm. Using electrostatic formalism, the Debye length can be described as the distance that perturbations from a charged "test" particle are felt. In a

plasma, we also can consider it the distance over which the plasma loses neutrality in order to screen the applied potential. Not surprisingly, the sheath thickness is typically a few to 100s of Debye lengths, depending on the voltage across the sheath.

Plasma Frequency

The fundamental frequency associated with a plasma is approximately the inverse of the time required for an electron to travel a Debye length. This time can be thought of as the time required for the electrons to shield the plasma from applied fields or charges. The frequency (in Hz) is density dependent and approximately given by:

$$f = 9000\sqrt{n}\,.$$

The use of frequency is instructive when considering the application of an rf field. If the applied field is at a frequency below the plasma frequency, the electrons can respond. For frequencies above the plasma frequency, they can not. It is similarly instructive to consider the ion plasma frequency, which is much smaller given the mass difference. This means the electrons can respond to frequencies ions can not, an important consideration when using rf biasing schemes.

Diffusion

The motion of charged species in plasmas is complicated. In the bulk plasma, particle motion is often dominated by collisions that serve to randomize particle trajectories. Isotropic motion is only possible in the absence of an electric field, and it depends on a particle's average velocity and mean free path. More often, however, this random motion is superimposed on a general drift introduced by the electric field. The difference in species mobility must be considered, but the motion of electrons strongly impacts the diffusion of all charged species. The less-mobile positive ions tend to retard the electron flow but in turn are dragged by them. Thus, the two species frequently leave the plasma at a rate governed by the ambipolar diffusion coefficient:

$$D_a = \frac{T_e}{e}\left(\frac{1}{\mu_i} + \frac{1}{\mu_i}\right)^{-1},$$

where μ_i and μ_e are the ion and electron mobilities, in units of $cm^2/V{\cdot}s$.

Types of Plasma Generation

Plasmas are formed when a gas is ionized, which is typically achieved by supplying energy to the gas via dc or rf electric fields. These fields initiate the plasma by accelerating stray electrons to energies sufficient for ionizing the background gas. Each ionization event forms an electron-ion pair, which provides electrons that can subsequently ionize additional gas species, quickly growing the number of electron-ion pairs. The plasma density thus rises dramatically until the ionization rate equals the ion and electron loss rate. At this point, the plasma has reached its steady-state plasma density and will remain there unless either the ionization or loss rates change. This chapter is mainly concerned with the steady state, although the application of pulsed plasmas in materials processing is common and can add processing capabilities.

A multitude of schemes have been developed to apply electric fields to a gas volume but generally, they are based on two approaches. The first is the application of power to a set of electrodes that are spaced some distance from one another, and it is the gas volume between these two plates that is excited, using either dc or rf power. Both cases will be discussed in further detail. The second approach involves applying power through an insulating surface, often a glass window that forms part of the vacuum chamber. Plasma sources of this type include inductively coupled plasmas (ICPs) that use an inductive coil driven by rf power, helicon reactors that also rely on rf power, and electron cyclotron resonance (ECR) discharges driven by microwaves. Other radiative sources include laser-driven plasmas and hollow cathodes. High-energy electron beams, which are not radiative, have been used as plasma sources also. The source of choice varies among the different processing communities, depending on needs that can be either materials or market driven. A summary of discharges used in processing is shown in Figure 2.

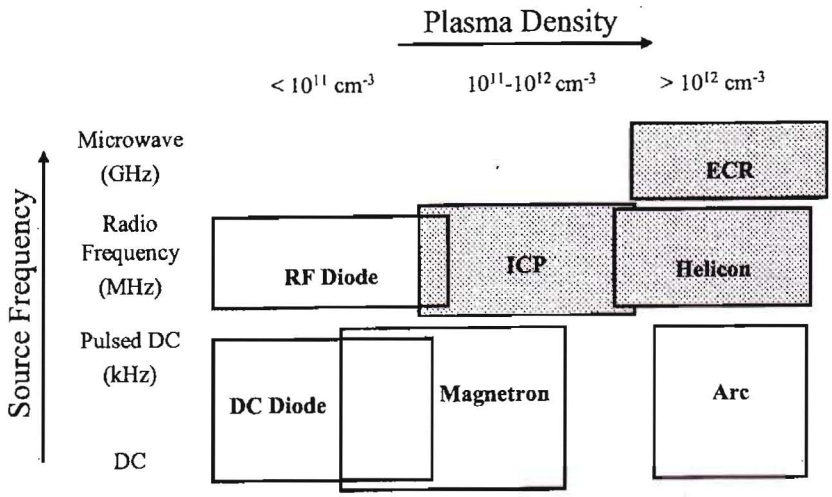

Figure 2. A sampling of sources used in materials processing. The sources are grouped roughly by applied power frequency and average plasma densities. The shaded sources have a lower incident ion energies at adjacent surfaces.

The dc Discharge

Perhaps the most well known type of plasma reactor is the dc diode discharge shown in Figure 3. Known more for their historical uses and simplicity than for their common use today, dc diodes consist of two parallel plates connected to a power supply. Plasma generation is governed by the Paschen relation, which indicates that for a given gas, pressure, and electrode separation, there exists a minimum voltage required to break down the gas. The dc discharge has a number of different operating modes, depending on the voltage, pressure, and distance between the electrodes. These discharges are usually inefficient plasma sources because the plasma is sustained by secondary electron emission at the cathode. Secondary electron emission induced by ion, photon, and metastable bombardment of the cathode, varies with cathode material, gas coverage, and incident energy but usually has a normalized yield that is much less than unity. Typically, for every electron that is emitted from the cathode, about 10 ions must hit the cathode. Another critical drawback for dc discharges is their limited capability in processing semiconductors or insulating materials. These materials restrict dc current flow, and any restriction in those currents would prohibit plasma production.

In etching or sputter deposition, high ion energy is normally required, and so the voltage drop across the sheath adjacent to the substrate is important to know. In the dc diode, the largest sheath potential is at the

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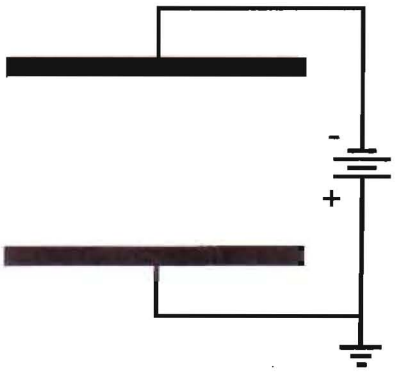

Figure 3. A simple dc discharge. A power supply is connected across two parallel plates. In this configuration, the top plate is the cathode, and the bottom plate is the anode.

cathode and where most of the ions leave the plasma. To understand why, consider a very simplified approach. First, recall that electrons have the highest mobility; alternatively this may be viewed as a lower resistivity than the ions. Also remember that the total current flow from the plasma will be zero, in steady state, so that:

$$j_i A_c \approx j_c A_a,$$

where j is the current density of each species, and A is the area of the cathode and anode. Lastly, assume the voltage drop across the cathode sheath can expressed as:

$$V_c = j_i R_i ,$$

where R_i is "ion resistance." A similar voltage drop across the anode sheath will be determined by electrons. For equal area electrodes then, the current densities will be equal, but the resistances will not, and so the cathode sheath voltage drop will be larger than the anode sheath voltage drop.

The rf Discharge

Rf diodes are similar to dc diodes in their geometry, but their operation is very different. Shown in Figure 4 is a simple rf diode, where a power supply is connected across parallel plates, and a capacitor is placed in series with the power supply. Although there is no rigid restriction on the rf frequency, sources are usually operated at a frequency above the ion plasma frequency, which is typically a few hundred kHz. At these frequencies, the electrons easily respond to the instantaneous fields, while the ions cannot. This means that during the positive swing of the applied voltage, electrons will accumulate on the electrode (the capacitor prevents charge from draining off, with or without an insulator on the electrode). During the negative swing, positive ions will accumulate on the electrode, but because of the lower mobility, not at the same rate, causing a net negative charge to accumulate. Here again, we find that the plasma potential will be positive with respect to the electrodes in order to ensure an equal ion and electron flow from the plasma. In this configuration however, the plasma potential will oscillate in response to the time-dependent charging, always remaining more positive than the most positive surface.

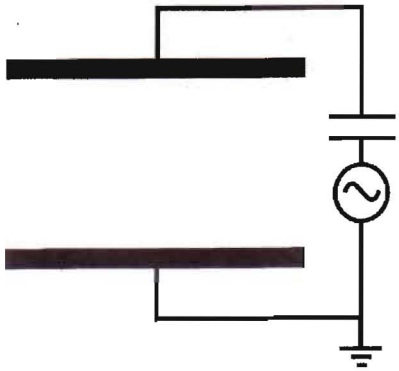

Figure 4. A capacity-coupled rf discharge. An rf power supply is connected across two parallel plates with a capacitor placed between the supply and the top (not grounded) plate.

Rf diodes are useful in processing semiconductor and insulating materials. In order to ensure a large voltage drop across one of the electrodes, the electrode on which the substrate should be placed, an asymmetric reactor geometry must be used, as shown in Figure 5.

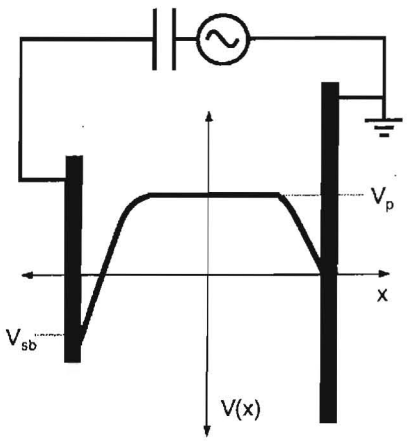

Figure 5. An asymmetric, parallel plate rf discharge along with the potential between the plates. This configuration allows for the establishment of a self-bias (Vsb) on the smaller driven electrode.

To understand this behavior, again consider the requirement:

$$j_d A_d = j_g A_g ,$$

where now j is the rf current density at the driven (d) and grounded (g) electrodes. If the areas are unequal, as shown in the Figure 5, we find:

$$\frac{A_d}{A_g} = \frac{j_g}{j_d} < 1 .$$

It follows then, that the larger rf current at the driven electrode results in a greater accumulation of negative charge on the driven electrode (the electrons are the dominant charge carriers). The result is larger electric field and thus potential on the driven electrode. This potential, called the dc self-bias (V_{sb}) since it develops in response to the applied rf, produces a larger incident ion energy at powered electrodes in these asymmetric reactors. The magnitude of the potential depends on the relative electrode area and applied rf power.

The Influence of Magnetic Fields

The use of magnetic fields in plasma sources is a powerful method to increase the utility of many sources. Planar magnetrons, for example, are much more efficient sputtering sources than simple dc diodes. To understand the utility of magnetic fields, recall the force on a charged particle in a magnetic field is given by:

$$F = qn \times B ,$$

causing the particle to travel in a radius, given by:

$$r = {mn_{\perp}}/{qB} ,$$

where B is the magnetic field, v is the velocity of the particle, and $v_{\perp}$ is the velocity perpendicular to the magnetic field. Because of the difference in mass, the magnetic field affects plasma electrons much more than it does the ions. For example, the ratio of radii of a hydrogen ion (1 amu) to an electron at the same energy would be $r(H^+)/r(e^-) = 43$. Because the electrons are strongly confined by the magnetic field, the ionization probability and thus plasma density are typically higher in magnetized sources.

Depending on the orientation, magnetic fields also reduce the conductivity of the plasma. Consider, for example, a magnetic field that is applied parallel to the electrodes in a dc diode, as shown in Figure 6. In this

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TiO (TITANIUM II OXIDE)	ASC-TIO		99.9%	1-3MM, 3-8MM	8X6MM	1 KG.	$325.
Ti2O3 (TITANIUM III OXIDE)	ASC-TI2O3		99.9%	1-3MM, 3-6MM	10X6MM	1 KG.	$520.
Ti3O5 (TITANIUM V OXIDE)	ASC-TI3O5	S-15-G	99.95%	0.5-3MM, 3-7MM	11X7MM	1 KG.	$520.
AL2O3 (ALUMINUM OXIDE)	ASC-AL2O3	S-8-G	99.99%	1-3MM		1 KG.	$312.
MgO (MAGNESIUM OXIDE)	ASC-MGO		99.9%	1-3MM		1 KG.	$645.
MgF2 (MAGNESIUM FLUORIDE)	ASC-MGF2		99.9%	.7-1.5MM, 1-3MM, 3-5MM, 5-8MM		1 KG.	$210.
HfO2 WHITE (HAFNIUM OXIDE)	ASC-HFO2		99.99%		10X5MM (TYPE FOR ZEISS COATING)	1 KG.	$975.
ZrO2 (ZIRCONIUM DIOXIDE WHITE)	ASC-ZRO2W	S-26-P	99.7%	1-3MM	13X6MM, 15X7MM, 19X7MM	1 KG.	$156.
ZrO2 (ZIRCONIUM DIOXIDE GREY)	ASC-ZRO2B	S-22-P	99.7%	1-3MM	12X6MM, 14X8 (ROUNDED PILL), 18X8MM	1 KG.	$338.
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Ta2O5 (TANTALUM PENTOXIDE)	ASC-TA2O5	TE-10	99.99%	1-3MM	10X3MM, 15X10MM	1 KG.	$980.
ITO (INDIUM TIN OXIDE) (90% In2O3, 10% SnO2)	ASC-ITO	SC-1-G	99.99%	1-3MM	7X6MM	100 GRAM	$225.
CHROMIUM	ASC-CRM	HSAK	99.5%	.7-1.5MM, 1-3MM, 3-5MM		1 KG.	$140.
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case, the electric (E) and magnetic (B) fields will be perpendicular, and a particle subject to these fields will gain a drift velocity ($v = (E \times B)/B^2$) that is also parallel to the plates. Thus it becomes more difficult for the currents to follow the electric field, and a reduction in conductivity follows. These arguments can be used to understand the magnetic field influence on ion diffusion because ambipolar diffusion is determined in part by the electrons. This of course, will depend on the direction of the magnetic field. Indeed, while diffusion perpendicular to the magnetic field will be reduced, diffusion parallel to the magnetic field will remain unchanged.

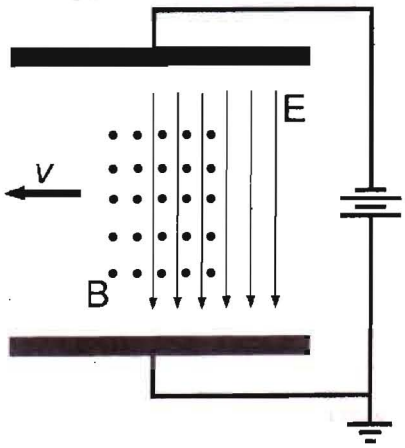

Figure 6. A parallel plate dc discharge with a magnetic field (dots) applied parallel to the plates. The magnetic field is perpendicular to the discharge electric field (arrows), causing a drift velocity (v) that is also parallel to the plates.

These concepts are useful in understanding the performance of planar magnetrons. By correctly orienting the magnetic field, the electrons are effectively caught in an "ExB loop" above the magnetron surface. This path leads to the formation of the doughnut-shaped, high-intensity plasma above the surface, the effects of which can easily be seen in the characteristic erosion track seen in used targets.

Plasma Chemistry

The transfer of power to the plasma electrons in a dc source is different from an rf source, but both utilize an electric field to raise the average electron energy. In most processing plasmas, the average energy is between 1 and 5 eV. Obviously, those values are not high enough to ionize many gases. However, the key to understanding ionization and the many processes that occur in the plasma is recognizing the breadth of the electron energies and the statistical nature of collisions with the gas molecules. While the average energy of the electrons might be low, the electron energy distribution will extend from very low energies up to large energies. The distribution function that describes the electron energies can take many forms but is often approximated by a Maxwellian distribution. In fact, for most processing plasmas, the distribution is far from Maxwellian and strongly dependent on the gas, particularly molecular gases that have a broad range of inelastic collisions.

Electron Heating and Cooling

Independent of how power is coupled to the plasma, electrons gain energy by being accelerated by the applied electric field. The method of applying the electric field does become important in defining the location of plasma generation. When applied across electrodes for example, the electrons are accelerated across the sheath and thus gain the energy over the sheath thickness. When fields are applied through dielectrics, the electrons are accelerated over the penetration volume called the skin depth (or resonance zones for ECRs).

Electrons are cooled either via wall losses, electrostatically, or through collisions. Wall loses cool the electron population by removing the most energetic electrons from the plasma because these are the only ones able to overcome the plasma potential. Electrostatic cooling describes the energy given up in the forming of the electric fields within the plasma or sheath. Note that much of this lost energy is transferred to the ions and removed from the plasma when the ions collide with adjacent electrodes. Collisional cooling proceeds through many different types interactions, as we shall see.

The establishment of the electron energy distribution is based on a balance between the heating and cooling mechanisms. For processing applications, one is most often interested in the average electron energy because it will determine the interactions between the plasma and any adjacent surface. Specifically, the average electron energy allows one to estimate the plasma potential and thus incident ion energy. The bulk of the electron-driven plasma chemistry, however, is determined by both the average energy and the shape of the distribution. Conversely, the average energy and shape of the distribution is often determined by the available electron-neutral processes. That is too say, electron collision processes both depend on *and* determine the electron energy distribution.

Electron-Neutral Reactions

The primary energy sink for electrons in molecular gases is inelastic electron-neutral collisions because little energy is transferred to the much larger molecules during elastic collisions. That is not to minimize the effect of elastic collisions on the electron population, which serve to randomize the velocity distribution of the electron population. While elastic collisions scatter the electrons, inelastic collisions cause a spread in their energy distribution.

There are several significant inelastic collisional processes to consider in plasmas. Although there is overlap, these reactions are listed roughly in order of the energy threshold:

Attachment: $e + AB \rightarrow AB^-$
Dissociative Attachment: $e + AB \rightarrow A + B^-$
Excitation: $e + AB \rightarrow AB^* + e$
Dissociation: $e + AB \rightarrow A + B + e$
Ionization: $e + AB \rightarrow AB^+ + e + e$
Dissociative Ionization: $e + AB \rightarrow A^+ + B + e + e$

The primary driver of plasma generation is of course ionization, which requires an electron energy in excess of the ionization potential, typically somewhere between 10 eV and 20 eV. In most discharges, the ionizing electron loses most of its kinetic energy during ionization because only a small fraction of electrons exceed the ionization potential by a significant amount. The ejected electron will have a similarly low kinetic energy.

Dissociation is particularly important in many processing plasmas since the radicals are often as or more important than the ions and parent molecules. In reactive deposition, O or N radicals formed from O_2 and N_2 are critical to the formation of metal-oxide or metal-nitride thin films. SF_6 and CF_4 are sources of F in surface fluorination and silicon etching. Dissociation of silane (SiH_4) and tetraethoxysilane {$Si(OCH_2CH_3)_4$} precursors are required in the deposition of silicon containing films in plasma-enhanced chemical vapor deposition (PECVD) processes.

Two processes that can have a significant impact on the plasma characteristics are electron attachment and excitation, both of which can have low thresholds. Attachment is common in electronegative gases like SF_6 and oxygen. The processes of attachment and dissociative attachment convert a fraction, sometimes a large fraction, of electrons to negative ions. This conversion can have a strong influence on the plasma characteristics, given the large mass difference between the negative ions and electrons and can lead to lower

conductivity. However, in most processing discharges, the attachment rate is too low to eliminate the dominance of electrons.

Excitation is of much greater importance because it is usually the dominant electron cooling mechanism and consumer of applied power. This is because it has the lowest energy threshold of all the processes (with the exception of electron-attachment in halogen gases). Moreover, excitation (which can lead to dissociation) is the dominant cross section up to several tens of electron volts.

To understand how the inelastic reactions listed above influence both electron cooling and power consumption, consider the nitrogen cross sections and their relationship to a typical Maxwellian electron energy distribution, all shown in Figure 7. Most electrons have energies below the ionization energy (15.6 eV), and thus most energy supplied to the plasma goes into exciting the gas rather than ionizing it. Note also that nitrogen has a sharp and unique peak in the excitation cross-section at about 2 eV. This would likely lead to a depression in the electron energy distribution at and above the peak energy. More simply, the distribution won't be Maxwellian.

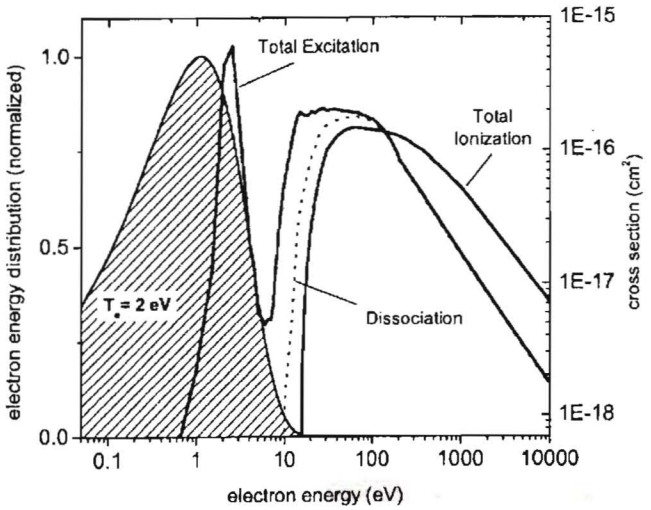

Figure 7. Electron-impact excitation, dissociation, and ionization of nitrogen (N2). Also shown is a Maxwellian electron energy distribution (shaded) with a temperature of 2 eV.

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Electron-Ion Reactions

Electron-ion recombination reactions are another important group of reactions and serve to reduce the plasma density. The rates of these reactions are quite fast for molecular ions and can thus strongly impact plasmas produced in molecular gases.

Heavy Particle Collisions

In addition to electron collisions, ions and radicals can react with each other or molecules within the plasma. The following reactions are common in many processing plasmas:

Resonant Charge Exchange:

$A^+ + A \rightarrow A + A^+$

$A^- + A \rightarrow A + A^-$

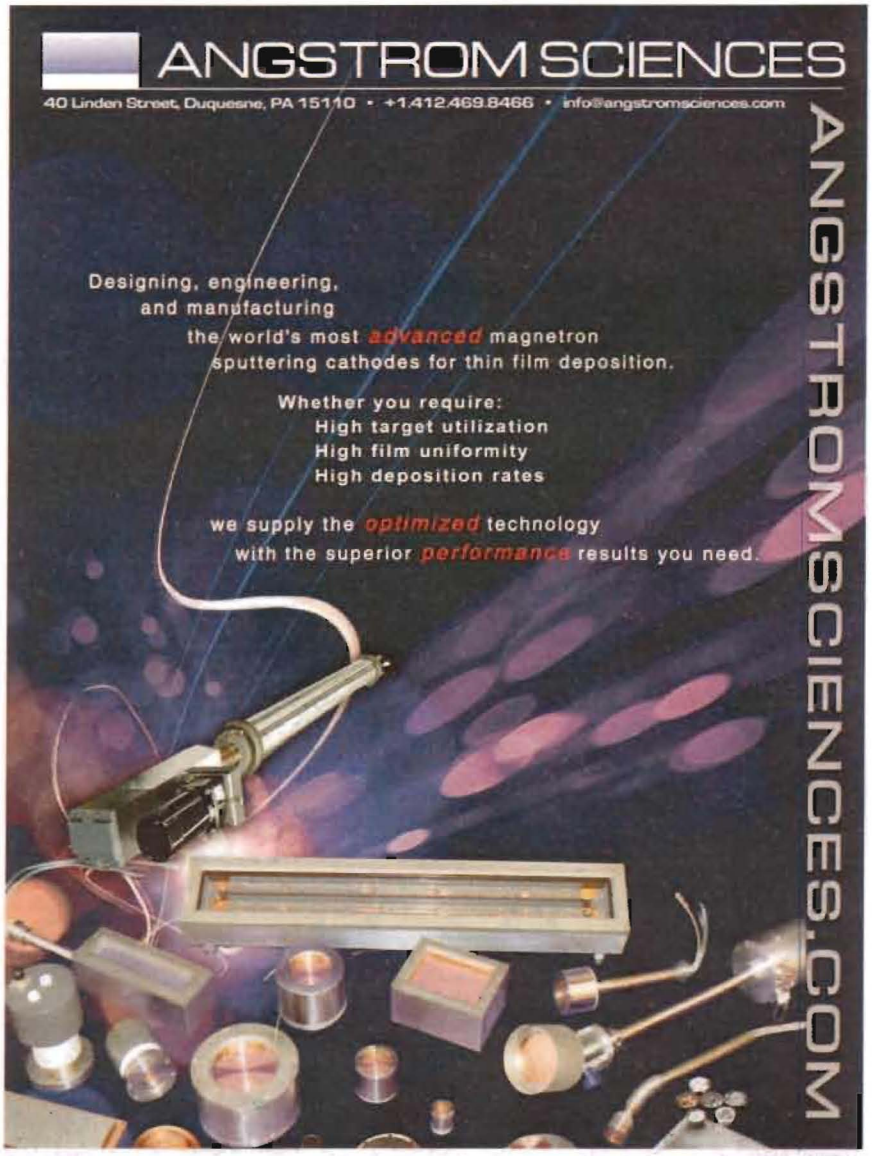
Non-resonant Charge Exchange:

$A^+ + B \rightarrow A + B^+$

$A^- + B \rightarrow A + B^-$

Recombination: $A^+ + B^- \rightarrow A + B^*$

The most common type of ion-neutral reactions is charge exchange, where the incoming ion is neutralized by an electron donated by the neutral target species, which is then ionized. If the ion energy is above room temperature, then the collision produces a slow ion and a fast neutral. Resonant charge exchange, which occurs between similar species, doesn't change the character of the charge species, but these reactions are important because the new ion effectively starts with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An Overview of Plasma Processes

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zero kinetic energy. This also ensures the ions will be accelerated in the direction of the electric field. This is why the energy distribution at surfaces can be quite broad in collisional sheaths but still highly anisotropic.

Non-resonant charge exchange reactions are similar to resonant charge exchange except that the reactions involve dissimilar species. In addition to creating a slow ion and fast neutral, the character of the positive ion and neutral species and possibly the reactivity of the plasma will be changed. In these collisions, electron exchange from molecule to atom is common, with rates that are very high.

As previously mentioned, plasmas produced in electronegative gases will have negative ion populations that may or may not be large. Some of the important reactions involving negative ions are ion-ion recombination and charge exchange reactions. Ion-ion recombination can be the largest loss of negative ions and like electron-ion recombination will reduce the plasma density. As with positive ions, charge exchange reactions involving negative ions are common and will be either resonant or non-resonant.

What's covered here barely scratches the surface in terms of the many specific reactions occurring in plasma. Indeed, materials processing can be quite complicated from a chemistry perspective. The introduction of multiple feedstock gases, large molecules, and surface reaction byproducts will all contribute to the gas phase reactions. At high pressures, one need also consider the possibility of three-body reactions. The above processes should, however, be considered as starting point when approaching the gas phase reactions in any processing plasma.

Plasma Processing: Past, Present, and Future

The use of plasmas in a broad range of materials processing applications is, at the very least, a testament to the benefits of using this so-called "fourth state of matter." They are an integral part in the production of so many things we, as a society, have come to take for granted. Things including the computer upon which this chapter was written, and the empty bag of potato chips that sits nearby. Beyond the everyday commodities, there are the truly life-altering applications in the field of biomaterials and medical device manufacturing that have benefited from plasma processing.

So why has plasma processing been so important in the development of so many materials? There are, of course, more reasons than space available to discuss, but some general reasons are clear. First, few other techniques have such a unique energy-delivering capability. Consider PECVD for example, where in the gas phase, plasma electrons are able to dissociate the precursor gases to produce reactive radicals and excited species. At the surface, energetic ions bombard the growing film. For the electrons, their kinetic energies are a few electron volts; for the ions, incident energies can be tens of electron volts. In terms of temperature, 1 eV is equivalent to 11, 429°K or roughly 40 times room temperature. This might not be as unique a property if it were not for the fact that the background gas and adjacent surface are *not* in thermal equilibrium with the plasma species; both the gas and surfaces can be maintained at room temperature. This enables the production of films at low gas and surface temperatures, which are advantageous for several substrate, gas, and film combinations.

The delivery of large fluxes of energetic ions to adjacent surfaces is perhaps one of the main advantages in plasma processing. This is particularly true in sputter deposition applications. The potential of plasmas to deliver a uniform flux over large areas is important in terms of material utilization and in industrial applications where throughput is of considerable importance. Sputtering of high-melting point and multi-component is also uniquely suited to the use of plasmas. Ions impacting adjacent surfaces, in the absence of any bias, will do so with energies approximately in the range of 5 to 25 eV, which is comparable to the sputtering threshold of many materials of interest. These thresholds are easily exceeded when target-basing techniques are applied and all of this energy is deposited within a few nanometers of the surface. All of this is difficult to achieve using non-plasma approaches.

Another advantage is the relative flexibility in producing plasma and plasma-based system for materials processing. As outlined, there are many approaches to plasma production, and each method has its advantages in terms of plasma characteristics. Additionally, there are a number of ways to enhance the processing conditions to meet the ever-evolving need to increase material attributes and performance. Looking again at sputter deposition, the development of rf or pulsed dc sputtering schemes was certainly hastened by the need to sputter insulating targets. The need to increase the ion flux at the substrate surface during sputter deposition, led to the development of the unbalanced magnetron and the idea of introducing a second plasma source close to the substrate.

In recent years, several interesting thrusts have emerged in the various processing communities. In the semiconductor industry, it is the development of dual-frequency plasma sources, where one frequency drives plasma generation, while the other controls incident ion energy. In an effort to curb expenses, many researchers are turning a favorable eye toward high-pressure plasma processing techniques in hopes of reducing capital and processing costs associated with maintaining vacuum. In the physical vapor deposition community, the development of high-power, pulsed magnetron sputtering is underway. There is also very interesting work in the development of micro-discharges for processing on the very small scale.

The past is often a reasonable predictor of what lies ahead, and given the rich and interwoven history of plasmas and materials processing, it is likely they will remain closely linked. The development of materials will continue to drive the technology of producing them and plasmas will remain part of that technology. Alternatively, the development of plasma sources will lead to the advent of novel materials. New directions are always hard to predict, but given the relatively narrow range of plasma characteristics that are presently employed in processing, many avenues are open for investigation.

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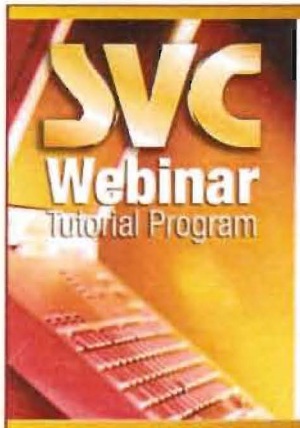

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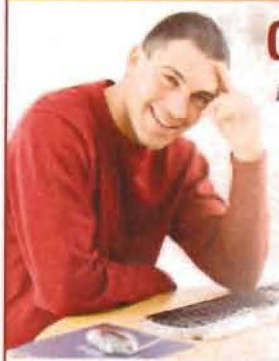

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